

PRICES SUBJECT TO CHANGE

ADD400186

N75-12078

THE EFFECT OF NEUTRON IRRADIATION ON THE
STRUCTURE AND MECHANICAL PROPERTIES OF
CARBON FIBRES

B. J. Wicks

March 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

19960312 065

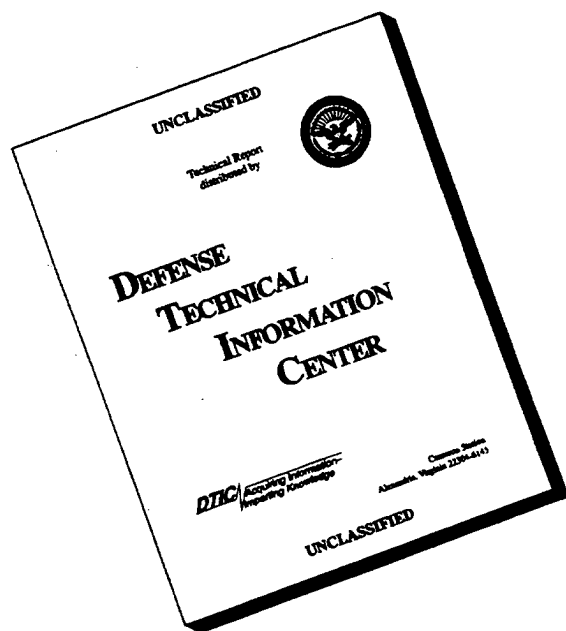
DTIC QUALITY INSPECTED 1

DISTRIBUTION STATEMENT 1

Approved for public release;
Distribution Unlimited

PLASTIC 22717

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.



**DEPARTMENT OF SUPPLY
AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
AERONAUTICAL RESEARCH LABORATORIES**

Metallurgy Report 93

**THE EFFECT OF NEUTRON IRRADIATION ON THE
STRUCTURE AND MECHANICAL PROPERTIES OF
CARBON FIBRES**

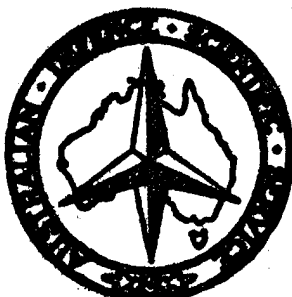
by

B. J. WICKS

(ARL/Met-REPT-93) THE EFFECT OF NEUTRON
IRRADIATION ON THE STRUCTURE AND
MECHANICAL PROPERTIES OF CARBON FIBRES
(Aeronautical Research Labs.)

N75-12078

Unclas
H2/24 03905



Reproduced by
**NATIONAL TECHNICAL
INFORMATION SERVICE**
US Department of Commerce
Springfield, VA. 22151

DOCUMENT CONTROL DATA

1. Security Grading/Release Limitation (a) Document Content Unclassified (b) This Page: Unclassified	2. Document Type/Number Metallurgy Report 93 3. Document Date March 1974
4. Title and Sub-Title THE EFFECT OF NEUTRON IRRADIATION ON THE STRUCTURES AND MECHANICAL PROPERTIES OF CARBON FIBRES	
5. Personal Author B. J. Wicks 6. Corporate Author(s)	
7. ABSTRACT <i>The effect of fast neutron irradiation on the mechanical and microstructural properties of carbon fibres heat-treated to various stages of graphitization has been investigated. Changes in selected crystallinity parameters were used to monitor the microstructural disorder induced in each fibre by three different irradiation doses. Associated changes in fracture strength and Young's modulus are related to the dependence of dislocation mobility on short-range microstructural damage.</i>	
8. Computer Program(s) — Titles and Language Not applicable	
9. Descriptors Carbon fibres Mechanical Properties Radiation damage Electron microscopy Composite materials Neutron irradiation Microstructure	11. Cosati Classifications 1105, 1808, 2002 12. Task Reference (RD/P) Supply 68/1
10. Library Distribution (Defence Group) A.R.L., G.A.F., D.S.L. (VIC). W.R.E. Vic. Region Central Office, Canberra Dept. of Defence:— Air-Engineering, Canberra Army-A.D.E.	13. Sponsoring Agency Reference — 14. Cost Code 32-800
15. Imprint AERONAUTICAL RESEARCH LABORATORIES	

PRICES SUBJECT TO CHANGE

DEPARTMENT OF SUPPLY
AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
AERONAUTICAL RESEARCH LABORATORIES

METALLURGY REPORT 93

THE EFFECT OF NEUTRON IRRADIATION ON THE STRUCTURE AND MECHANICAL PROPERTIES OF CARBON FIBRES

by
B. J. WICKS

SUMMARY

The effect of fast neutron irradiation on the mechanical and microstructural properties of carbon fibres heat-treated to various stages of graphitization has been investigated. Changes in selected crystallinity parameters were used to monitor the microstructural disorder induced in each fibre type by three different irradiation doses. Associated changes in fracture strength and Young's modulus are related to the dependence of dislocation mobility on short-range microstructural damage.

CONTENTS

	Page No.
1. INTRODUCTION	3
2. EXPERIMENTAL	3
3. EFFECTS OF FAST NEUTRON IRRADIATION	4
3.1 Changes in Mechanical Properties	4
3.2 Changes in Crystallinity Parameters	5
3.3 Microstructural Changes	5
4. THE EFFECT OF NASCENT HYDROGEN	6
5. DISCUSSION	6
6. CONCLUSIONS	8
ACKNOWLEDGEMENTS	9
REFERENCES	9
TABLE 1	
TABLE 2	
TABLE 3	
FIGURES	
DISTRIBUTION	
DOCUMENT CONTROL DATA	

1. INTRODUCTION

Small doses of fast neutrons have been found to enhance the mechanical strength and modulus of bulk reactor graphite by up to a factor of two, although exposure to higher doses results in relatively small additional improvements¹. A considerable effort has been directed towards producing carbon fibres with superior mechanical characteristics using graphitizing heat treatments which are known to modify structural perfection². This paper describes the effect of potentially damaging environments, using neutron irradiation as one example, on the microstructure and mechanical performance of single carbon fibres.

Unlike most reactor graphites, which consist of well-crystallized, relatively randomly oriented polycrystalline aggregates, carbon fibres derive their inherently high mechanical properties from a highly oriented, relatively poorly graphitized, layer structure^{3,4}.

Since the tolerance of the carbon structure to damage by neutron irradiation depends on the alignment of the anisotropic graphite layers¹, the stability of the textured fibre structure is expected to differ significantly from that of isotropic bulk graphites.

A model of the carbon fibre structure, which is used later to discuss the effects of neutron irradiation, has been proposed on the basis of microstructural observations⁵. A three-dimensional representation of this model (Fig. 1) depicts continuous graphite layers having a random stacking sequence in the 'c' direction and a highly preferred orientation parallel to the fibre axis. Regions of crystallinity are separated, in a longitudinal direction, by zones of extensive bending and twisting of the basal layers at tilt, twist and bend plane boundaries which consist of arrays of basal dislocations. Sharp-edged microvoids separate adjacent crystalline regions in the transverse direction. The effect of graphitizing treatments at elevated temperatures ($> 1000^{\circ}\text{C}$) is viewed as a progressive elimination of these boundaries by migration and annihilation resulting in increased crystalline order.

In macroscopically isotropic, polycrystalline graphites the effects of radiation damage on mechanical performance are particularly sensitive to grain size and irradiation temperature⁶. Anisotropic changes in crystallite dimensions on irradiation show an obvious correlation with the crystallinity of the unirradiated structure, viz., shrinkage parallel to the graphite basal planes and a simultaneous expansion normal to these planes.

Carbon fibres heat-treated to high tensile strength (i.e. at 1600°C) increase significantly in strength and stiffness after moderate irradiation (doses of 2×10^{17} n.v.t.)⁷. Fibres graphitized at higher temperatures, which produce a higher modulus, suffer progressive structural degradation, as measured by specific crystallinity parameters, after high neutron radiation doses⁸; fracture strength and modulus are also deleteriously affected.

The sensitivity of mechanical properties to changes in the microstructure of polyacrylonitrile-based carbon fibres has been investigated, using graphitizing heat-treatments to induce long-range ordering in the alignment of graphite layer planes². The present study sought to elucidate the factors which determine the tolerance of the mechanical properties of carbon fibres to short-range microstructural damage. Attempts were made to inter-relate the structural and mechanical effects of fast neutron irradiation, over a range of neutron exposures, for fibres heat-treated to three different degrees of crystallinity. The effects of hydrogen-charging on the mechanical and structural properties were also studied as another means of inducing short range damage.

2. EXPERIMENTAL

All carbon fibres used in this study were produced from polyacrylonitrile precursors according to the basic R.A.E. patented process³. Two of the fibre types, designated HT and HM, were supplied by Morganite Modmor. The third, designated PAN 70, was manufactured in collaboration with Weapons Research Establishment, South Australia. The fibre types were designated according to their stages of graphitization, as determined by the final heat-treatment temperature, viz. (i) HT— 1600°C (ii) HM— 2500°C (iii) PAN 70— 3000°C . The third fibre type exhibited the largest

surface flaws and internal voids, with consequently lower average strength and modulus properties. Variations in the strength and modulus of these fibres, together with relevant microstructural details, are described elsewhere⁸.

Fibres were tested for ultimate strength and static Young's modulus, before and after irradiation using an Instron machine with a 50 g load cell. Each fibre was suspended between fine glass end-grips, to which it was attached by thermosetting adhesive. This arrangement minimised extraneous disturbances from air currents and vibrations.

The microstructural changes produced by point defect damage were examined by transmission electron microscopy using a Philips E.M.200. Specimens were prepared by polishing fibres in an oxy-hydrogen flame⁹.

X-ray studies were made by irradiating aligned fibre bundles with CuK_α x-rays in a Philips 57 mm diameter powder camera. For accurate line broadening and preferred orientation measurements, a powder diffractometer was used to examine a number of fibres mounted in parallel on a frame. Comparative crystallite sizes (L) were determined from the corrected peak width of reflections from the two-dimensional turbostratic lattice, using the relation¹⁰

$$L = \frac{0.92 \lambda}{\beta \cos \theta}$$

where β represents the width of the reflection peak at half maximum intensity (in radians), λ is the x-ray wavelength and θ is the Bragg diffraction angle. Although no corrections were made for distortion broadening, the values derived are sufficiently precise to enable relative comparison of the variations in preferred orientation, interlayer spacing and crystallite size.

Fibre bundles in each heat-treatment condition were separated from the same tow to facilitate comparisons. Each bundle was packed in aluminium powder in an aluminium can, then inserted into a second aluminium can which was subsequently sealed and irradiated in the hollow fuel element position in the Heavy Water Materials Testing Reactor (HIFAR) at the Australian Atomic Energy Commission, Lucas Heights. The irradiation temperature was in the range 75–100°C.

Fast neutron doses were measured using titanium flux monitors in each can. An absorption cross-section of 12 mb for the $^{46}\text{Ti}(n, p)^{46}\text{Sc}$ was used to calculate the integrated fast neutron fluxes from the measured ^{46}Sc activities, and the results quoted relate to energies greater than 1 MeV. The 12 mb cross-section is based on the neutron energy spectrum of the HIFAR reactor.

3. EFFECTS OF FAST NEUTRON IRRADIATION

3.1 Changes in Mechanical Properties

The results of tensile tests on single fibres, for the three stages of graphitization (i.e. heat treatment at 1600°C, 2500°C and 3000°C) in the unirradiated state and irradiated to doses of 1.0×10^{17} n.v.t., 1.5×10^{19} n.v.t. and 7.0×10^{19} n.v.t. ($E > 1$ MeV) are presented in Fig. 2. Both fracture stress and static Young's modulus were measured at each radiation dose level, with at least 40 tests on each fibre condition.

Student t tests of significance were used to estimate the degree of confidence in the measured property changes. The observed strength and modulus variations are at high levels of significance for the 1600°C and 2500°C heat-treated fibres. Using the 2500°C heat-treatment as an example, fast neutron irradiation initially increases modulus ($t = 3.8$ for 91 degrees of freedom), and strength ($t = 3.7$ for 91 degrees of freedom). Prolonged exposure degrades fibre performance, with a subsequent decrease in both stiffness ($t = 7.5$ for 89 degrees of freedom) and strength ($t = 1.3$ for 89 degrees of freedom). At the highest dose the modulus decreases below the unirradiated value, although a degree of strengthening is retained. For the HT fibres, the variations in modulus were also at consistently higher levels of significance than the strength values.

Although the PAN 70 fibre exhibited a wide scatter in individual measurements, the observed variations in modulus were still at high levels of significance, with an initial increase ($t = 3.9$ for 88 degrees of freedom) being followed by a degradation ($t = 5.1$ for 90 degrees of freedom). The changes in tensile strength were at much lower levels of significance, with $t = 1.7$ for 86 degrees of freedom and $t = 0.7$ for 90 degrees of freedom being associated with the apparent improvement and deterioration respectively. Structural examination of PAN 70 fibres in the unirradiated state suggested a probable link between the poor mechanical performance, the wide

scatter in property measurements, and the observed variability in crystallinity along fibre lengths, with the frequent occurrence of severe stress-raising flaws.

The sensitivities of both tensile strengths and moduli to radiation damage follow a similar trend, indicating that changes in bulk properties of the fibres could be responsible. The susceptibility of mechanical properties to irradiation strongly depends on the perfection of the internal structure formed during heat-treatment. Thus, the neutron dose required to induce maximum strength and stiffness increases with increasing crystallinity; highly graphitized fibres attain maximum strength and stiffness at higher doses than poorly graphitized fibres heat treated at lower temperatures.

3.2 Changes in Crystallinity Parameters

Crystallinity parameters measured for each irradiation condition are shown in Table 1, together with the values before irradiation. The parameters selected, viz., the apparent crystallite dimension (L_c) in the c direction, the interlayer spacing (d_{002}) and the degree of preferred alignment of graphitic layers (ϕ) with respect to the fibre axis, are presented with the corresponding strength and modulus values.

Radiation-induced changes in the crystallinity parameters show well-defined trends with increasing radiation dose, characterized by (1) a decrease in crystallite size and (2) a reduction in the preferred alignment of basal layers along the fibre axis.

Although an increase in inter-layer spacing can be discerned at intermediate doses in the irradiation programme received by the low modulus fibres, marked changes in the inter-layer spacings of HM fibres are only observed at the highest dose level; low and intermediate doses cause only minor lattice expansions in the c direction. A similar trend is apparent in the fibres graphitized to 3000°C. A reverse trend in inter-layer spacings with increasing doses has been observed elsewhere in high modulus fibres⁸, and it is possible that the insensitivity of lattice spacings to irradiation damage observed here for HM fibres is a related phenomenon. It is likely that the effect is associated with internal stresses along layer planes, resulting from an accumulation of lattice sites. The tendency for layer planes to shrink during irradiation leads to a redistribution of crystallite boundaries by migration and annihilation, tending to relax layers to the unirradiated spacing. In low modulus fibres the higher concentrations of boundaries and imperfections within layer planes form effective sites for dislocation locking, thus preventing the relief of internal stresses.

3.3 Microstructural Changes

The microstructural effects of fast-neutron irradiation were investigated by transmission electron microscopy. The microstructure of an unirradiated fibre (Fig. 3(a)) is similar to that described elsewhere⁹, viz., chains of reflecting zones, identified with packets of parallel basal layers which are aligned preferentially along the fibre axis; each reflecting zone or crystallite is separated from its neighbours by elongated microvoids in the transverse direction and by sharp intercrystalline boundaries in the longitudinal direction.

The structure of such fibres is basically unaffected by irradiation. At the highest radiation dose (Fig. 3(b)) the main distinction appears to be a more diffuse boundary associated with each reflecting zone, making resolution of adjacent zones more difficult. No evidence was obtained at any flux level for the formation of voids or dislocation loops, such as could result from an aggregation of point defects formed by displacement damage. The distribution and dimensions of platelets which have previously been identified as ordered graphite¹¹ were determined to be unchanged by irradiation.

Frequency distributions of strength values in fibres graphitized at 1600°C and 2500°C, before and after irradiation to 7.0×10^{19} n.v.t. are recorded as histograms in Fig. 4. No significant alteration in the frequency distribution of breaking stresses and moduli of fibres is apparent, although any modification of the spatial distributions of stress-raising flaws in the fibres should be reflected in the distribution of mechanical properties. It is therefore concluded that no new macroscopic flaws are introduced into the fibre by irradiation. The fact that changes in both strength and modulus induced by irradiation are of similar magnitude at each dose level is further evidence for this conclusion. Since the evidence presented shows that neither the formation

of stress-raising flaws nor changes in the distribution of pre-existing flaws is responsible, it is concluded that the observed variation in mechanical properties of carbon fibres must be interpreted in terms of microstructural damage.

4. THE EFFECT OF NASCENT HYDROGEN

It is well known that free hydrogen atoms diffuse readily into metals to produce hydrogen embrittlement. In view of the marked effect of irradiation, presumably associated with displacement damage, on the mechanical properties of carbon fibres, an attempt was made to simulate the introduction of point defects by introducing free hydrogen.

Two free-hydrogen environments were used to affect the mechanical properties of carbon fibres. In one experiment, high modulus fibres were immersed in 20% hydrochloric acid for extended periods. In the second experiment, a bundle of fibres formed the cathode of an electrolytic cell, consisting of a bulk carbon anode and a 20% hydrochloric acid electrolyte. Immersion periods of 75 hours and 200 hours were used in each environment. The results (Table 2) show that the fracture strengths of carbon fibres are relatively unaffected by prolonged exposure to free hydrogen. The modulus is markedly reduced, particularly after a 200 hour exposure ($t = 4.3$ for 61 degrees of freedom). The dilute acid solution has less effect on modulus than the electrolytic cell, for the exposure used.

Table 2 also shows that the changes in mechanical properties are associated with a reduction in crystallite size and a increase in interlayer spacing. The degree of preferred alignment of basal layers is unaffected by contact with these environments.

Microscopic observation shows that relatively short exposures (up to 10 hours) in concentrated hydrochloric acid produce swelling at the fibre ends, over lengths of approximately twice the fibre diameter.

5. DISCUSSION

Radiation damage in fibres should occur by the simple displacement phenomena observed in bulk graphites. Atoms which are displaced by collisions with incident neutrons can remain as isolated point defects, aggregate to form dislocation loops or coalesced interlayer clusters, or disappear at structural defects. Depletion of either vacancies or interstitials by the last mechanism is the principal cause of macroscopic dimensional changes in bulk graphite. Thus, the distribution of point-defect traps and sinks in the initial microstructure should largely determine both the form and the amount of radiation damage which is retained.

Previous studies of irradiated carbon fibres have established that mechanical properties may be influenced by competing processes involving atomic displacements and radiation-enhanced oxidation¹². The latter mechanism provides vacant surface lattice sites which may combine with the internal displaced atoms, depending on the temperature of irradiation. In the present study no evidence for surface oxidation could be obtained, using scanning electron microscopy, for the fibre batches studied. Moreover, for the temperature of irradiation used here ($< 100^\circ\text{C}$) the limited mobility of point defects is very unlikely to allow significant recombination at free surfaces¹³. It is therefore considered that the effect of displacement damage alone has been isolated.

The observed changes in fibre modulus after neutron irradiation can be explained in terms of the greater mobility of interstitials compared with vacancies in the graphite structure. At the temperature of irradiation used in this study, vacant lattice sites are 'frozen' in the structure, while single interstitial defects are relatively mobile because of their lower activation energy for migration. Unassociated interstitials will therefore be assimilated at traps, such as dislocation boundaries, within the basal sheets or at the microvoids between adjacent crystallite zones. These traps act either as heterogeneous nucleation sites for interstitial clusters, or as sinks which can absorb interstitials. The degree of reduction in point defect damage depends on the spatial distribution of microvoids or boundaries, i.e. on the effective crystallite dimensions.

For the fibres used here, the crystallite size parameter L_c has been shown to increase progressively with increasing graphitization temperature up to 2500°C (Table 3)³. Thus, at the low doses which generate isolated point defects, interstitials should be removed faster in fibres graphitized at lower temperatures. Due to the ensuing reduced concentration of interstitial point defects, the probability of recombination of vacancy-interstitial pairs is substantially reduced, and a higher degree of damage is retained in low modulus fibres. In fibres of higher modulus and

larger crystallite size, the probability of interstitial-vacancy recombination is also higher and, thus, a similar accumulation of point-defect damage is delayed until higher doses.

The radiation-induced increase in static modulus at low doses is attributed to a pinning of glissile basal dislocations within graphitized regions. A large component of the dynamic modulus of carbon fibres in the unirradiated state has been identified with dislocation movement¹⁴, and an interaction between dislocations and point defects has been proposed to explain the influence of impurities on the modulus of carbon fibres⁷. As the contribution of dislocation motion to the modulus of irradiated fibres decreases, the effective shear constant, c_{44} , of the component crystallites tends towards the "single-crystal" value of the turbostratic graphite structure. An additional mechanism, a coupling between neighbouring basal planes formed by the bonding between di-interstitial atoms in adjacent basal layers, could similarly increase the measured fibre modulus; such a mechanism is known to affect the modulus of irradiated pyrolytic graphite¹⁵.

Under continued irradiation, the supersaturation of interstitial point defects within crystallites eventually reaches a level at which homogeneous nucleation of interstitial clusters occurs. The neutron dose at which this critical supersaturation is reached will depend on the crystallite size; coalescence of point defects will be delayed to higher doses in well-graphitized fibres. Such interlayer clusters will cause gross dimensional changes in the crystallites of carbon fibres, similar to the dimensional changes in bulk graphites during neutron irradiation. Distortion of basal layers by interlayer clusters is first detected as a decrease in preferred orientation, a decrease in effective crystallite dimensions and an increase in interlayer spacing. Structural degradation associated with this irradiation level is responsible for a reduction in Young's modulus as the effective elastic shear constant of the lattice is decreased. This interpretation is consistent with the observation that the doses at which the crystallinity parameters begin to change significantly coincide with the onset of deterioration in mechanical properties.

Fracture strengths of the carbon fibres have been identified with specific defects in the structure¹¹. Platelets of three-dimensionally ordered graphite are dispersed in random orientations throughout the body of the fibre which consists predominantly of turbostratic graphite. The relationship between platelet size and fibre strength is similar to that expected if the platelets act as pre-existing Griffith cracks¹⁶, and it is proposed that crack initiation occurs at those platelets which are most favourably oriented with respect to the stress axis.

In this study the dimensions and distribution of these platelets have been found to be unchanged by irradiation. Moreover, since the distribution of breaking strengths and fibre moduli remains essentially unaffected by irradiation, and the observed variation in both strength and modulus follows a similar trend, it is concluded that the distribution of stress-raising flaws is unaffected by irradiation to these flux levels; Mrozowski cracks were not detected by microstructural examination. Thus, although fibre fracture is initiated by stress concentrations at transversely aligned platelets, the variations in fracture strength due to fast neutron irradiation are associated with changes in the fibre structure, and not with changes in the dimensions or distributions of pre-existing flaws.

In assessing the significance of the observed variations in strength, consideration must be given to the effects of the observed changes in modulus on the stress required for crack propagation. Such consideration requires comparison of the effective work of fracture for the different structural states. Evidence for changes in the work of fracture with irradiation is provided by the variations in the parameter F (Table 3), the elastic strain energy at fracture, which is calculated from,

$$F = \frac{\sigma_f^2}{2E}$$

and, using the Griffith formula,

$$F \propto \frac{\gamma}{c}$$

where σ_f is the fracture stress, E the observed modulus and c the size of the initial flaw. The parameter F is a relative measure of the variation in the effective surface energy for fracture (γ) since it has been demonstrated above that, in a given fibre type, pre-existing stress-raising flaws responsible for fibre fracture are unaffected by neutron irradiation.

The value of F decreases at low doses for all fibre categories. This trend is reversed at higher doses and, at the highest recorded dose, F is significantly above the unirradiated values. Previous measurements of platelet sizes in carbon fibres subjected to various graphitizing heat treatments¹⁶

enable a calculation of the absolute values of effective work of fracture; these platelets are considered to act virtually as pre-existing Griffith cracks because of their weak interlayer bonding. The absolute values of γ necessarily exhibit similar variations to F for each type of fibre, but there is no obvious means of gaining additional understanding from an absolute comparison of the different fibres.

It is proposed that the major factor contributing to the initial effect of irradiation is a general increase in resistance to the mobility of basal dislocations, which reduces plastic flow at the tip of microstructural stress concentrators, thus decreasing the effective work of fracture. A decrease in the mobility of dislocations would be consistent with the observed increase in modulus at low doses.

The only alternative explanation, viz. that the irradiation-induced point defects directly affect the surface energy for fracture by changing the number of carbon-carbon bonds which have to be broken by a propagating crack, seems unlikely as the predicted effects are too small to account for the observed variations.

The rate of accumulation of point defect damage at low neutron doses has been calculated for nuclear graphite, giving a net vacancy creation rate of 1.3×10^{-21} per unit neutron flux density¹⁷. A similar rate of accumulation in carbon fibres would yield an induced vacancy concentration of approximately $10^{-3}\%$ of atomic sites after irradiation to the dose at which the greatest reduction in surface energy occurs. The surface energy for fracture should be reduced by the same proportion, assuming that the surface energy depends on the number of carbon-carbon bonds in graphite layers which have to be ruptured per unit area of fractured surface. This decrease is so much less than the actual decrease ($\approx 10\%$) that this mechanism can be disregarded as a contributor to the initial effect of irradiation.

It is also proposed that the major contribution to the increased surface energy terms at the highest dose level is from an increase in the density of mobile dislocations formed from the radiation-induced damage. These dislocations would operate by adding a plastic component to the energy required to propagate an expanding crack front. This explanation is reinforced by the known dislocations in fibres doped or irradiated to produce low concentrations of point defects⁷. An increase in the density of mobile dislocations at high doses is also consistent with the reduction in moduli to values less than those of unirradiated fibres.

The alternative explanation, that interlayer clusters can increase the surface energy term, can be shown to be inadequate. At the highest neutron dose, approximately 10% of atoms could occupy interstitial positions in the fibre structure, based on the assumed rate of accumulation of point defects. Even if all these atoms form interlayer clusters and the number of carbon-carbon bonds which have to be broken by an advancing crack front could increase by the same proportion, the effect would be insignificant compared to an estimated increase in surface energy of approximately 30% (Table 3(b)). Thus this explanation is inadequate to account for the effects of high neutron doses, and the previous explanation for the change in surface energy is favoured.

The effect of nascent hydrogen on the mechanical properties of carbon fibres is attributed to a similar mechanism. Introduction of atomic hydrogen into the fibre structure is believed to result in the accumulation of molecular hydrogen at interstitial voids, leading to the enlargement of these voids and to disturbances of layer plane alignments. Such effects would be reflected in reduced strength and modulus values, as observed.

6. CONCLUSIONS

- (a) The effect of fast-neutron irradiation on the mechanical properties of carbon fibres, heat-treated to different stages of graphitization, has been determined. All fibres initially increase in strength and modulus, at low and intermediate doses, but reductions in strength and modulus occur at high doses. The dose at which the maximum values are attained increases with the degree of graphitization.
- (b) Structural changes accompanying neutron damage are characterized by (i) a reduction in the preferred orientation of graphitic layers (ii) a decrease in crystallite size (iii) an increase in interlayer spacing. Appreciable changes are observed only at doses greater than those which induce optimum mechanical properties.
- (c) Changes in mechanical properties by radiation damage are explained on the basis of two competing processes, viz. (i) the mobility of basal dislocations is reduced by point-defect

damage, the predominant effect at low doses, and (ii) the increase in dislocation density and misalignment of graphite layers, which predominates at high doses. Changes in fibre strength are related to changes in the energy required to propagate cracks from pre-existing platelets of graphite.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. K. D. Reeve of the Australian Atomic Energy Commission for arranging the irradiation programmes for the fibres used in this study.

REFERENCES

1. Taylor, R., Brown R. G., Gilchrist, K., Hall, E., Dodds, A. T., Kelly, B. T., and Morris, F. Carbon, (1967), 5, 519.
2. Johnson, W., Phillips, L. N., and Watt, W. Brit. Patent 1,110,791.
3. Coyle, R. A., Gillin, L. M., and Wicks, B. J. J. Aust. Ceramic Soc., (1970), 6, 29.
4. Coyle, R. A., and Gillin, L. M. Aeronautical Research Laboratories Met. Note 63, 1969.
5. Wicks, B. J., Coyle, R. A., and Gillin, L. M. Proceedings of the Tenth Biennial Conference on Carbon (1971).
6. Thrower, P. A. Carbon, (1968), 6, 687.
7. Cooper, G. A., and Mayer, R. M. J. Materials Science, (1971), 6, 60.
8. Jones, B. F., and Peggs, I. D. J. Nuclear Materials, (1971), 70, 1591.
9. Wicks, B. J. J. Materials Science, (1971), 6, 173.
10. Warren, B. E. Phys. Rev., (1941), 59, 693.
11. Coyle, R. A., Gillin, L. M., and Wicks, B. J. Nature, (1970), 226, 257.
12. Bullock, R. E. J. Materials Science, (1972), 7, 964.
13. Thrower, P. A., and Loader, R. T. Proceedings of the Ninth Biennial Conference on Carbon (1969), p. 212.
14. Curtis, G. J., Milne, J., and Reynolds, W. N. Nature, (1968), 220, 1024.
15. Goggin, P. R. Nature, (1963), 199, 367.
16. Coyle, R. A., and Wicks, B. J. Aeronautical Research Laboratories Met. Note 98, 1974.
17. Thompson, M. W., and Wright, S. B. J. Nuclear Materials, (1965), 16, 146.

Postal Address: Chief Superintendent,
Aeronautical Research Laboratories,
P.O. Box 4331,
MELBOURNE, Victoria 3001

TABLE 1

Variations in mechanical properties and structural parameters (preferred orientation ϕ , crystallite size L_c and inter-layer spacing d_{002}) with fast-neutron dose for different stages of graphitization. Average tensile strength ($\bar{\sigma}$) and modulus (\bar{E}) values are shown with the corresponding standard deviation(s) at each dose level.

Neutron Dose		Tensile Strength		Young's Modulus		ϕ°	L_c (Å)	d_{002} (Å)
		$\bar{\sigma}$ (10^3 p.s.i.)	s	\bar{E} (10^6 p.s.i.)	s			
HT	unirradiated	410	113	34.6	3.5	36	21	3.49
	1.0×10^{17} n.v.t.	450	133	43.8	8.6	35	19	3.49
	1.5×10^{18} n.v.t.	422	102	37.7	4.3	40	16	3.64
	7.0×10^{19} n.v.t.	430	137	29.3	3.8	39	14	3.74
HM	unirradiated	235	86	60.8	9.7	15	68	3.40
	1.0×10^{17} n.v.t.	236	92	67.8	8.4	15	64	3.41
	1.5×10^{18} n.v.t.	314	112	68.4	9.8	16	52	3.43
	7.0×10^{19} n.v.t.	287	102	53.8	8.5	19	41	3.54
PAN 70	unirradiated	104	48	34.9	9.8	15	65	3.41
	1.0×10^{17} n.v.t.	92	48	38.5	14.8	21	64	3.43
	1.5×10^{18} n.v.t.	122	52	45.4	15.3	20	55	3.46
	7.0×10^{19} n.v.t.	114	54	33.4	9.2	21	35	3.53

TABLE 2

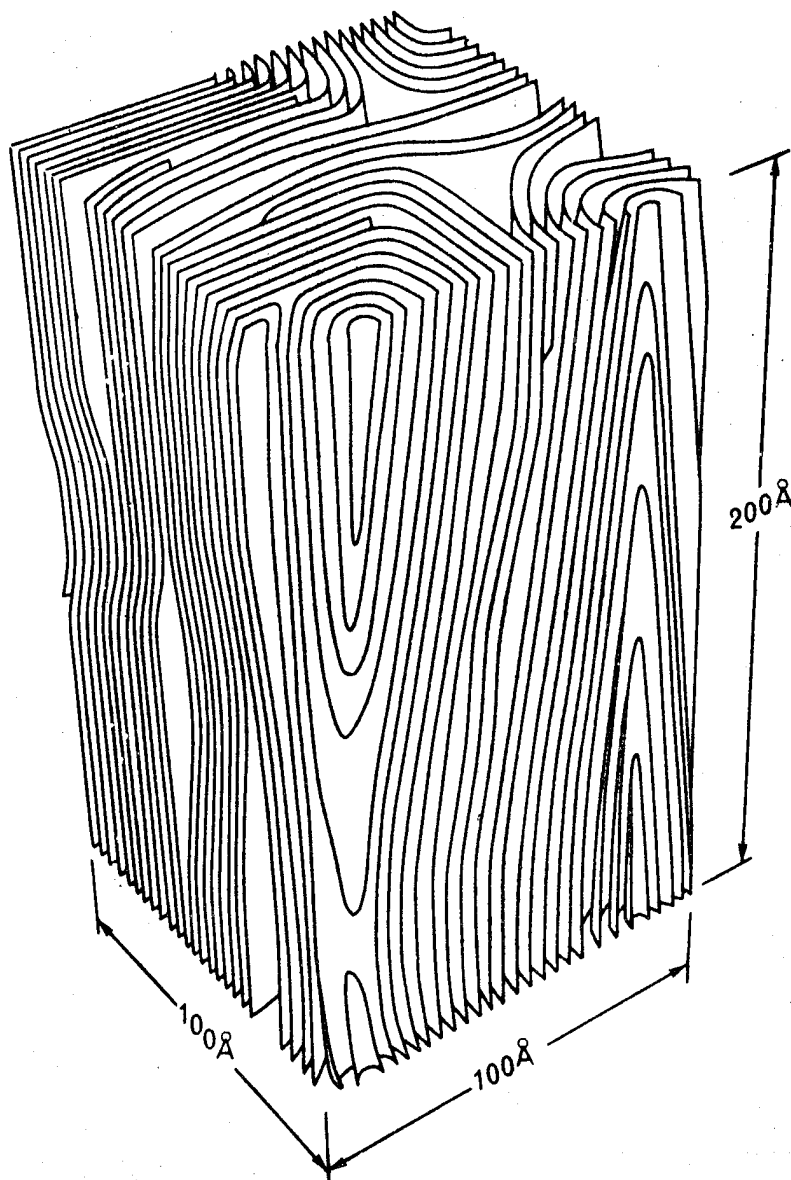
The effect of exposure to hydrogen on the strength and modulus of carbon fibres for two periods of time. Changes in crystallinity parameters (preferred orientation ϕ , crystallite size L_c and inter-layer spacing d_{002}) are recorded after the longer period. Mean values of tensile strength ($\bar{\sigma}$) and modulus (\bar{E}) are recorded for each treatment along with the corresponding standard deviations (s).

Treatment	75 Hours				200 Hours							
	Tensile Strength		Modulus		Tensile Strength		Modulus		ϕ°	$L_c(\text{\AA})$	$d_{002}(\text{\AA})$	
	$\sigma(\times 10^3\text{p.s.i.})$	s	$E(\times 10^3\text{p.s.i.})$	s	$\sigma(\times 10^3\text{p.s.i.})$	s	$E(\times 10^3\text{p.s.i.})$	s				
Untreated Acid Immersion Electrolytic Charging	235	86	61	9.7	235	86	61	9.7	19	60	3.42	
	219	71	62	4.5	218	68	56	11.0	19	54	3.44	
	220	32	53	4.1	218	65	51	8.3	19	53	3.44	

TABLE 3

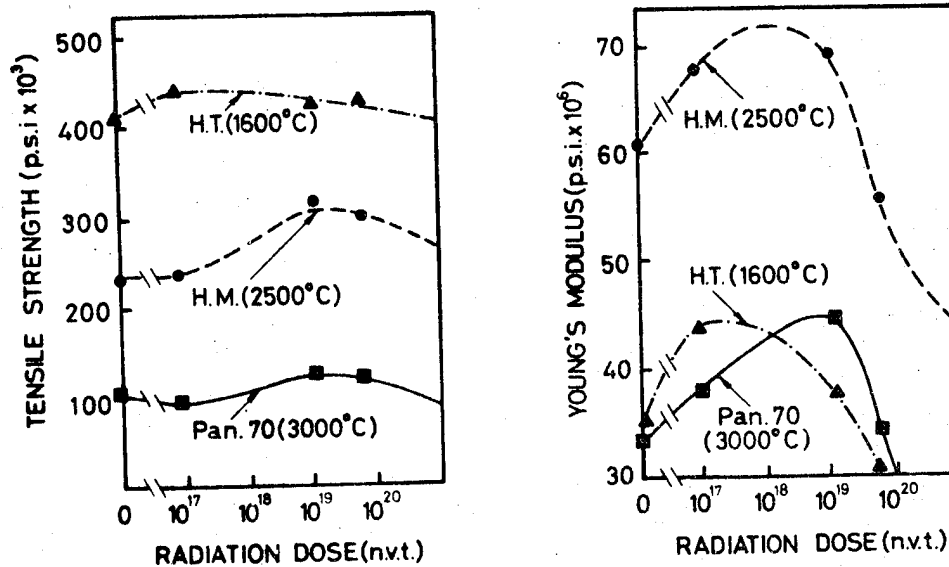
Values of elastic strain energy per unit volume at fracture F , and effective surface energy γ , calculated from a simple Griffith relationship at various neutron dose levels for different types of carbon fibre. The values of γ are calculated from relevant values of F , assuming that observed platelets of graphite in irradiated fibres act as Griffith cracks in initiating fracture.

Irradiation Dose (n.v.t.)	Graphitization Temperature ($^\circ\text{C}$)					
	1600		2500		3000	
	$F(\text{J/m}^3)$	$\gamma(\text{J/m}^2)$	$F(\text{J/m}^3)$	$\gamma(\text{J/m}^2)$	$F(\text{J/m}^3)$	$\gamma(\text{J/m}^2)$
unirradiated	16.7	0.59	3.13	0.41	1.07	0.32
1.0×10^{17}	15.1	0.53	2.82	0.37	0.76	0.23
1.5×10^{19}	16.3	0.57	4.96	0.65	1.07	0.32
7.0×10^{19}	21.8	0.76	5.28	0.69	1.34	0.40



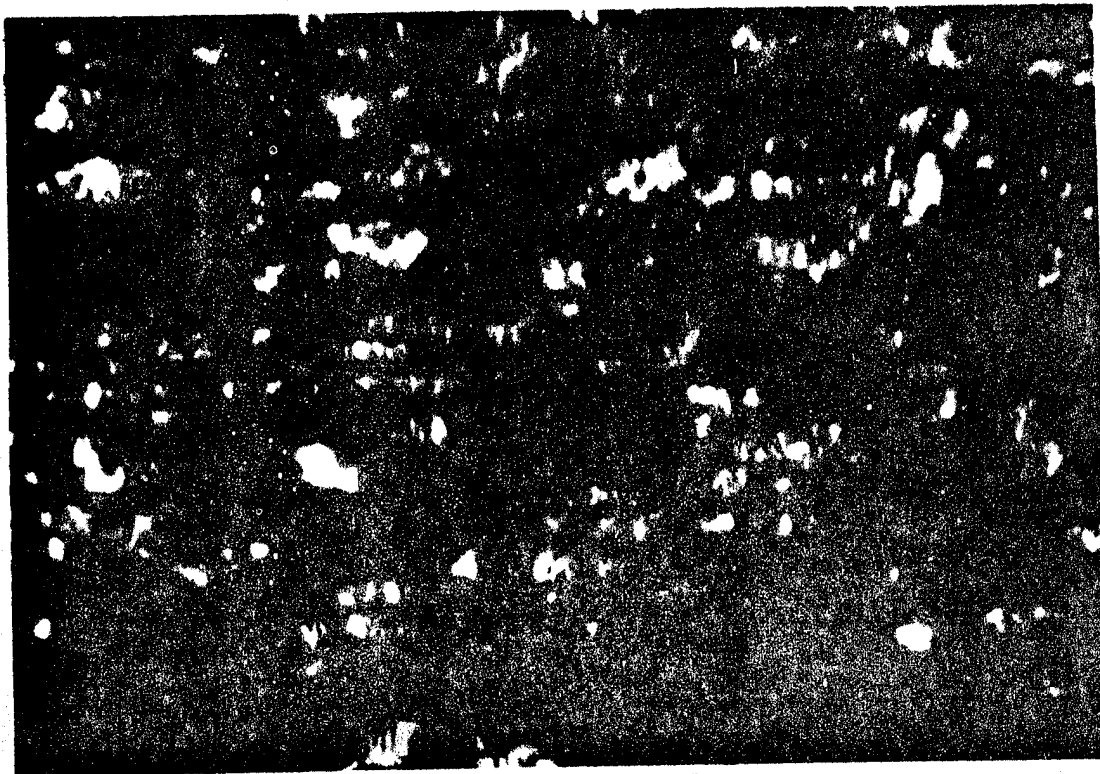
REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

SCHEMATIC THREE-DIMENSIONAL MODEL OF THE CARBON FIBRE
STRUCTURE. THE FIBRE AXIS IS SHOWN BY THE ARROW.

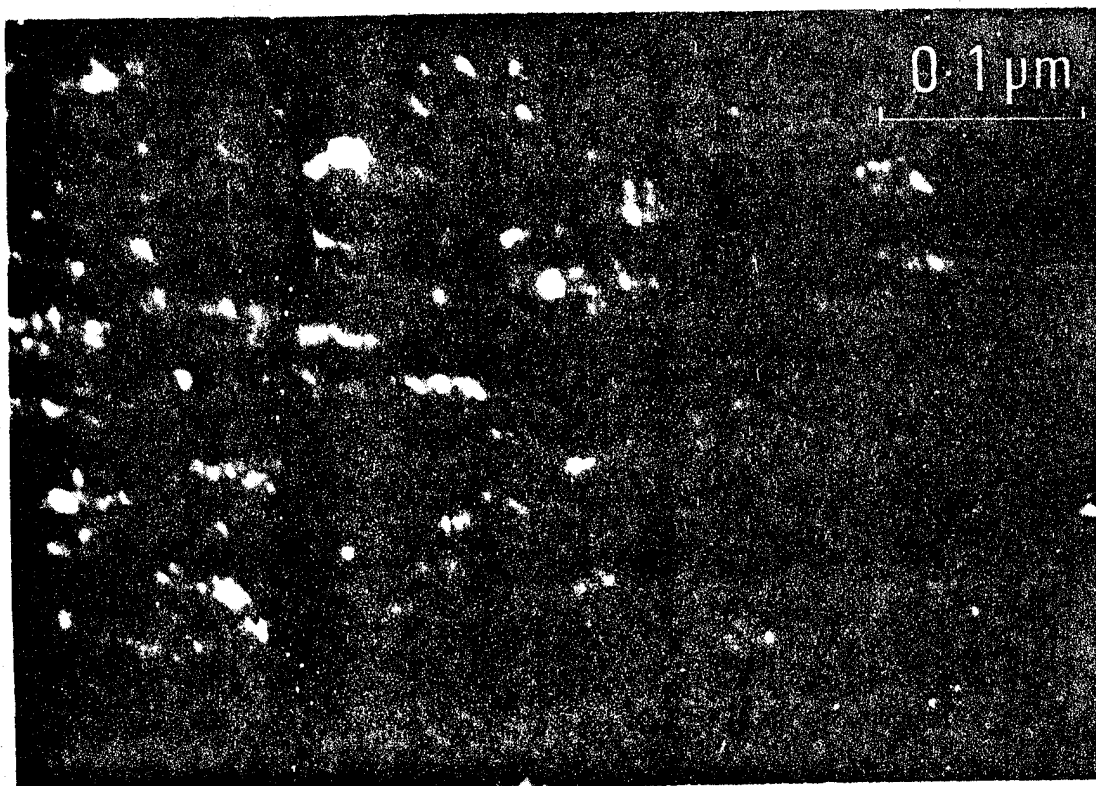


REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

THE EFFECT OF FAST NEUTRON IRRADIATION ON THE YOUNG'S
MODULUS AND STRENGTH OF PAN BASED CARBON FIBRES GRAPHITIZED
TO THE TEMPERATURES SHOWN.

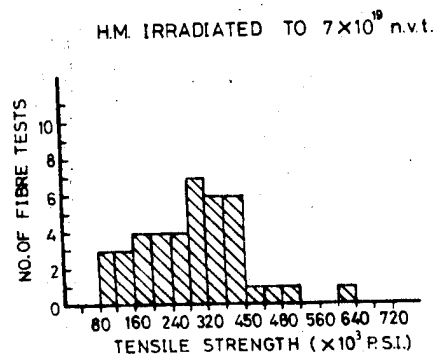
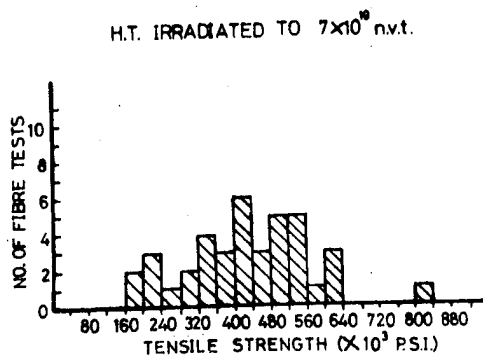
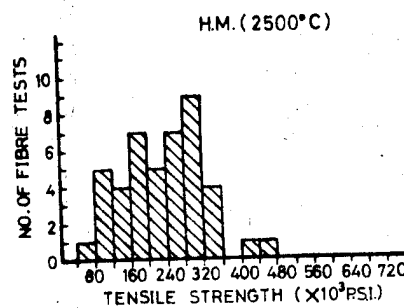
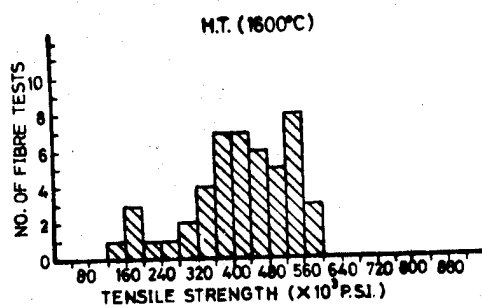


(a)



(b)

TRANSMISSION ELECTRON MICROGRAPHS TAKEN UNDER DART-FIELD
CONDITIONS USING THE (002) BASAL PLANE REFLECTION OF (A)
UNIRRADIATED HM FIBRE (B) HM FIBRE IRRADIATED TO 7.0×10^{19} n.v.t.



REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

HISTOGRAMS SHOWING THE FREQUENCY DISTRIBUTIONS OF TENSILE
STRENGTH OF HT AND HM FIBRES BEFORE AND AFTER IRRADIATION TO
 7.0×10^{19} n.v.t.